

We Claim:

1. A pultrusion process for preparing a cured fiber reinforced composite comprising the steps of:
- a) pulling continuous fibers through an impregnation die;
 - b) supplying a polyol component and a polyisocyanate component to produce a reaction mixture and feeding the reaction mixture to the impregnation die;
 - c) contacting the fibers with the reaction mixture in the impregnation die for a time period and at a temperature sufficient to cause substantial polymerization of the reaction mixture within the impregnation die to produce a composite of fibers coated by the reaction mixture;
 - d) directing the composite of coated fibers through a heated curing die to at least partially advance the cure of the reaction mixture so as to produce a solid fiber reinforced polymer matrix; and
 - e) drawing the solid composite from the curing die, wherein the reaction mixture gels between 340 and 768 seconds at 25°C and between 95 and 210 seconds at 140°C.
2. The pultrusion process according to Claim 1, wherein the polyol component and the isocyanate component are mixed using a static mixer.
3. The pultrusion process according to Claim 1, wherein the polyol component contains one or more catalysts suitable for promoting at least one reaction selected from the group consisting of the reaction of isocyanate groups with alcohol groups to form urethane bonds, and the trimerization of isocyanate groups to form isocyanurate groups.
4. The pultrusion process according to Claim 1, wherein the fibers and the reaction mixture are supplied concurrently to the impregnation die.
5. The pultrusion process according to Claim 1, wherein the curing die includes a plurality of zones having different temperatures.
6. A solid composite product produced according to the process of Claim 1.

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7. The solid composite product according to Claim 6, wherein the polymer matrix contains a plurality of urethane groups formed from the reaction of the polyol component and the polyisocyanate component.
- 5 8. The solid composite product according to Claim 6, wherein the polymer matrix contains a plurality of isocyanurate groups, the isocyanurate groups formed from the trimerization of isocyanate groups present in the polyisocyanate component.
9. A reaction system for the preparation of a fiber reinforced composite in a pultrusion process, the reaction system comprising:
- 10 a) a liquid reaction mixture formed by combining a polyol component and a polyisocyanate component; and
- b) a continuous fiber reinforcing material; wherein the liquid reaction mixture initially contains both free isocyanate groups and free alcoholic -OH groups, and gels between 340 and 768 seconds at 25°C and between 95 and 210 seconds at 140°C.
- 15 10. The reaction system according to Claim 9, wherein the reaction mixture contains release agent.
- 20 11. The reaction system according to Claim 9, wherein the reaction mixture contains one or more catalysts suitable for promoting at least one reaction selected from the group consisting of the reaction of isocyanate groups with alcohol groups to form urethane bonds, and the trimerization of isocyanate groups to form isocyanurate groups.
- 25 12. The reaction system according to Claim 9, wherein the Index of the reaction mixture is from 200 to 1000 and the reaction mixture contains at least one catalyst for the trimerization of isocyanate groups.
- 30 13. The pultrusion process according to Claim 1, wherein the polyol component and the polyisocyanate component are mixed at an Index of from 200 to 1000, and the polyol component contains at least one catalyst for the trimerization of isocyanate groups.

14. The reaction system according to Claim 9, wherein the Index of the reaction mixture is less than 200.

15. The pultrusion process according to Claim 1, wherein the Index of the reaction mixture is less than 200.

16. The reaction system according to Claim 9, wherein the reaction mixture is devoid of amines.

10 17. The reaction system according to Claim 16, wherein the reaction mixture contains metal carboxylate release agent.

18. The reaction system according to Claim 17, wherein the metal carboxylate release agent is selected from the group consisting of zinc stearate, calcium stearate, and mixtures of thereof.

19. A solid composite product produced according to the pultrusion process of Claim 1, wherein the solid composite has a specific gravity, measured according to ASTM D 792, of from 1.43 to 1.44.

20. The pultrusion process according to Claim 1, wherein the reaction mixture contains phosphate release agent.

21. The reaction system according to Claim 9, wherein the reaction mixture contains phosphate release agent.

22. The pultrusion process according to Claim 1, wherein the polyol component comprises an aromatic polyester polyol.

23. The reaction system according to Claim 9, wherein the reaction mixture contains aromatic polyester polyol.

24. The pultrusion process according to Claim 1, wherein the polyisocyanate component comprises isocyanate terminated prepolymer.

25. The reaction system according to Claim 9, wherein the reaction mixture comprises isocyanate terminated prepolymer.

26. A pultrusion process for preparing a cured fiber reinforced composite comprising the steps of:

- a) pulling continuous fibers through an impregnation die;
- b) supplying a polyol component and a polyisocyanate component to produce a reaction mixture and feeding the reaction mixture to the impregnation die;
- c) contacting the fibers with the reaction mixture in the impregnation die for a time period and at a temperature sufficient to cause substantial polymerization of the reaction mixture within the impregnation die to produce a composite of fibers coated by the reaction mixture;
- d) directing the composite of coated fibers through a heated curing die to at least partially advance the cure of the reaction mixture so as to produce a solid fiber reinforced polymer matrix; and
- e) drawing the solid composite from the curing die, wherein the reaction mixture contains release agent selected from the group consisting of fatty amides, fatty esters, fatty acids, and mixtures thereof.

27. A pultrusion process for preparing a cured fiber reinforced composite comprising the steps of:

- a) pulling continuous fibers through an impregnation die;
- b) supplying a polyol component and a polyisocyanate component to produce a reaction mixture and feeding the reaction mixture to the impregnation die;
- c) contacting the fibers with the reaction mixture in the impregnation die for a time period and at a temperature sufficient to cause substantial polymerization of the reaction mixture within the impregnation die to produce a composite of fibers coated by the reaction mixture;

d) directing the composite of coated fibers through a heated curing die to at least partially advance the cure of the reaction mixture so as to produce a solid fiber reinforced polymer matrix; and

e) drawing the solid composite from the curing die, wherein the reaction mixture
5 contains release agent selected from the group consisting of erucamide, stearamide, oleic acid, one or more fatty ester reaction products of adipic acid with pentaerythritol and oleic acid, the reaction products having acid number less than 15 and hydroxyl number less than 15, caruba wax, beeswax, butyl stearate, octyl stearate, ethylene glycol monostearate, ethylene glycol distearate, glycerine monooleate, dioctyl sebacate, one or more metal
10 carboxylates, one or more silicones, montan wax, one or more hydrocarbons having from 10 to 19 carbon atoms, polytetrafluoroethylene, one or more phosphates, one or more chlorinated phosphates, and mixtures thereof.

28. The pultrusion process according to Claim 27, wherein the release agent comprises at
15 least one member selected from the group consisting of zinc stearate and calcium stearate.

29. The pultrusion process according to Claim 27, wherein the reaction mixture is devoid of amines.

30. The pultrusion process according to Claim 27, wherein the polyol component and the
20 polyisocyanate component are mixed at an Index of from 200 to 1000, and the polyol component contains at least one catalyst for the trimerization of isocyanate groups.

31. The pultrusion process according to Claim 27, wherein the reaction mixture comprises
25 aromatic polyester polyol.

32. The pultrusion process according to Claim 30, wherein the reaction mixture comprises aromatic polyester polyol.

33. The pultrusion process according to Claim 27, wherein the polyisocyanate component
30 comprises isocyanate terminated prepolymer.

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34. The pultrusion process according to Claim 30, wherein the polyisocyanate component comprises isocyanate terminated prepolymer.

35. A pultrusion process for preparing a cured fiber reinforced composite comprising the steps of:

- a) pulling continuous fibers through an impregnation die;
- b) supplying a polyol component and a polyisocyanate component to produce a reaction mixture and feeding the reaction mixture to the impregnation die;
- c) contacting the fibers with the reaction mixture in the impregnation die for a time period and at a temperature sufficient to cause substantial polymerization of the reaction mixture within the impregnation die to produce a composite of fibers coated by the reaction mixture;
- d) directing the composite of coated fibers through a heated curing die to at least partially advance the cure of the reaction mixture so as to produce a solid fiber reinforced polymer matrix; and
- e) drawing the solid composite from the curing die, wherein the reaction mixture has a gel time in the range of 84 to 600 seconds when maintained at 23°C, and the reaction mixture cures within 1 minute when heated to a cure temperature in the range of 120 to 140°C.

36. A pultrusion process for preparing a cured fiber reinforced composite comprising the steps of:

- a) pulling continuous fibers through an impregnation die;
- b) supplying a polyol component and a polyisocyanate component to produce a reaction mixture and feeding the reaction mixture to the impregnation die;
- c) contacting the fibers with the reaction mixture in the impregnation die for a time period and at a temperature sufficient to cause substantial polymerization of the reaction mixture within the impregnation die to produce a composite of fibers coated by the reaction mixture;
- d) directing the composite of coated fibers through a heated curing die to at least partially advance the cure of the reaction mixture so as to produce a solid fiber reinforced polymer matrix; and

e) drawing the solid composite from the curing die, wherein the polyol component contains a catalyst for the trimerization of isocyanate groups, the polyol component and the polyisocyanate component are combined to produce an Index of between 300 and 900, the reaction mixture has a gel time in the range of 84 to 600 seconds when maintained at 23°C, and the reaction mixture cures within 1 minute when heated to a cure temperature in the range of 120 to 140°C.

37. The pultrusion process according to Claim 35, wherein the polyol component comprises polyester polyol.

38. The pultrusion process according to Claim 36, wherein the polyol component comprises polyester polyol.

39. A reaction system suitable for the preparation of a fiber reinforced composite by means of a pultrusion process comprising:

a) a liquid reaction mixture formed by combining a polyol component and a polyisocyanate component; and

b) a continuous fiber reinforcing material, wherein the liquid reaction mixture initially contains both free isocyanate groups and free alcoholic -OH groups, has a gel time in the range of 84 to 600 seconds when maintained at 23°C, and cures within 1 minute when heated to a cure temperature in the range of 120 to 140°C.

40. A polyisocyanurate fiber reinforced composite formed from the reaction system of Claim 39.

41. The reaction system according to Claim 39, wherein the reaction mixture comprises at least one member selected from the group consisting of fatty ester release agent, phosphate release agent, wax release agent, fatty amide release agent, hydrocarbon release agent having from 10 to 19 carbon atoms, polyester polyol, metal carboxylate release agent, and mixtures thereof.

42. The reaction system according to Claim 39, wherein the polyisocyanate component comprises isocyanate terminated prepolymer.

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43. The reaction system according to Claim 39, wherein the polyisocyanate component is a mixture of 2,4'-MDI, 4,4'-MDI, and pMDI, having about 19.5% by weight 2,4'-MDI, 60.9% by weight 4,4'-MDI, and 19.6% by weight pMDI, and having an NCO value of 32.5.
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44. The reaction system according to Claim 39, wherein the polyisocyanate component comprises uretonimine modified MDI.
45. The reaction system according to Claim 39, wherein the polyisocyanate component
- 10 comprises polymeric MDI.
46. The reaction system according to Claim 39, wherein the reaction mixture contains alkali carboxylate catalyst.
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47. The reaction system according to Claim 39, wherein the alkali carboxylate catalyst comprises a potassium carboxylate.
48. The reaction system according to Claim 39, wherein the reaction mixture contains a blocked amine catalyst.
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49. The reaction system according to Claim 39, wherein the reaction mixture contains a tertiary amine catalyst.